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# Conformational and Energetic Properties of the Ammonia Dimer—Comparison of Post-Hartree–Fock and Density Functional Methods

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MARTINA KIENINGER and SÁNDOR SUHAI\*

Department of Molecular Biophysics, German Cancer Research Center, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany

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## ABSTRACT

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The equilibrium structure of the ammonia dimer has been investigated with density functional and MP2 calculations. We used Slater- and Becke-exchange functionals combined with correlation functionals as recommended by Vosko–Wilk–Nusair, by Perdew, and by Lee–Yang–Parr, respectively. The potential energy surfaces was investigated. The asymmetric cyclic “microwave” structure could be identified as a minimum. Optimization of the intermolecular parameters showed that this structure has nearly the same energy as the centrosymmetric cyclic structure. Full optimization transformed the asymmetric cyclic structure into the linear structure. The interaction energies in the dimer were corrected for the basis set superposition error using the Boys–Bernardi counterpoise method and the *a priori* chemical Hamiltonian approach, respectively. © 1996 by John Wiley & Sons, Inc.

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## Introduction

**D**ensity functional methods have, in the past, been applied mainly to extended systems like metal surfaces, clusters, and semiconductor compounds. In the last few years, however, they

have been tested to describe the properties of small organic compounds.<sup>1,2</sup> Part of the research was dedicated to the investigation of hydrogen-bonded complexes<sup>3–7</sup> due to their importance in biological systems. Recent studies using density functional theory (DFT) cover the region from strong to weak hydrogen bonds.<sup>4–6</sup> Among these complexes the ammonia dimer can be regarded as an especially sensitive test for the quality of *ab initio* calculations.

\* Author to whom all correspondence should be addressed.

For a long time the ammonia dimer was believed to belong to complexes forming a classical linear hydrogen bond. This was substantiated by early theoretical calculations.<sup>8-11</sup> Most of the calculations assuming a linear hydrogen bond employed relatively small basis sets. It was later shown by Latajka and Scheiner<sup>12</sup> and Del Bene<sup>13</sup> that the equilibrium geometry of the ammonia dimer is extremely sensitive to the size of the basis set used.

Due to the experimental work of Klemperer and coworkers,<sup>14-16</sup> the cyclic structures of the ammonia dimer also drew the attention of theoretical investigators. Inspired by their work, Latajka and Scheiner<sup>17</sup> calculated the potential energy surface of the ammonia dimer, which was only a function of the two intermolecular rotational angles at the SCF level using a 4-31G\* basis set. The linear and the cyclic minima on that surface were then optimized at the MP2 level using a 6-31G\*\* basis set. Latajka and Scheiner claimed that the centrosymmetric structure, which has a dipole moment near zero, should be more stable than the linear one with a dipole moment of about 2-3 D. This was confirmed by Hassett et al.<sup>18</sup> who employed a smaller basis set. Using an extended basis set, Hassett et al., however, found the cyclic structure to be a transition state which is only about 0.04 kcal/mol less stable than the eclipsed linear one.

The dipole moment found by Klemperer and coworkers in their work from 1985,<sup>14-16</sup> about 0.75 D, contradicts, however, both the centrosymmetric cyclic (about 0 D) and the linear (2-3 D) structures. In addition, Klemperer et al. performed rotational spectroscopic experiments on a series of ammonia van der Waals complexes.<sup>19</sup> These investigations show that ammonia does not denote a hydrogen to form a hydrogen bond in these complexes. Supported by gas-phase high resolution spectra, Klemperer and coworkers suggested an asymmetric "microwave" cyclic structure.<sup>12-14</sup> This suggestion was supported by the work of Sagarik and coworkers who performed a series of calculations on a set of 75 ammonia dimer configurations at both the SCF and the CPF (coupled pair functional) levels, predicting this "microwave" asymmetric cyclic structure as the equilibrium one.<sup>20</sup>

However, recent far-infrared and microwave spectra by Loeser et al.<sup>21</sup> and calculations based on them by van Bladel et al.<sup>22</sup> indicate that the "microwave" structure is unlikely to be the equilibrium one. Frisch et al. determined that the staggered quasilinear structure is only 0.2 kcal/mol

more stable than the centrosymmetric cyclic structure.<sup>23</sup> This prediction was confirmed by a full geometry optimization at the MP2 level using the 6-311 + G(*d*, *p*) basis set.<sup>24</sup>

Finally, Tao and Klemperer<sup>25</sup> stressed in their work the fact that an exact equilibrium structure is difficult to determine due to the extreme flatness of the lowest potential energy path connecting the linear and the cyclic structures. Taking corrections to the basis set superposition error (BSSE) into account and using midpoint bond functions, their results suggest that a cyclic structure is the equilibrium one. Tao and Klemperer also emphasize the importance of the dispersion energy in the ammonia dimer. This is in agreement with several other investigations<sup>26-28</sup> and shows that, besides the basis set, correlation energy plays a key role in determining the equilibrium configuration and the interaction energy of the ammonia dimer. Therefore, it can be expected that the DFT will be especially useful for the study of this complex.

DFT calculations using local and nonlocal exchange correlation potentials were performed for the first time by Zhu and Yang<sup>6</sup> for selected structures of the ammonia dimer. They found the linear structure to be by about 0.8 kcal/mol more stable than the cyclic one. They also reported intermolecular distances which are too small when using the simple local potential and which were comparable to MP2 results when calculated with the gradient-corrected one. These observations are in agreement with the results of Sim et al.,<sup>3</sup> who found a similar behavior for the water dimer and for other hydrogen-bonded complexes.

Numerous recent calculations dedicated to hydrogen-bonded complexes point out that the Slater-exchange-Vosko-Wilk-Nusair (VWN) correlation potential yields intermolecular distances, which are too short.<sup>3-7</sup> Perdew, Becke-Perdew (BP), and Becke-Perdew-Yang-Parr (BPYP)-gradient-corrected potentials give, on the other hand, distances which agree with experimental results and MP2 calculations. To investigate which contribution to the total energy is responsible for this behavior we performed a series of calculations by varying the intermolecular distance in the cyclic and in the linear structure of the ammonia dimer.

BSSE on the hydrogen-bonding energies were corrected with the Boys-Bernardi counterpoise method<sup>29,30</sup> as well as with the "chemical Hamiltonian approach" (CHA).<sup>31-33</sup> The implementation of this method within DFT has recently been reported.<sup>34</sup> To investigate the potential energy surface of the intermolecular rotational movements of

the ammonia dimer we performed a second series of calculations.

Similar to the investigations of Latajka and Scheiner,<sup>17</sup> we varied the two intermolecular angles from 0° to 180° with a fixed intermolecular distance as shown in Figure 1. We obtained a potential energy surface which also allows insight into the description of the dispersion energy with the chosen density functionals.

Finally, we investigated the asymmetric cyclic structures of the ammonia dimer which appear on the potential energy surface with all three functionals used. For this purpose, we performed optimizations of the intermolecular geometry parameters starting from the asymmetric as well as from the centrosymmetric cyclic structures. The DFT results were confirmed by MP2 calculations using the same basis sets.

## Methods

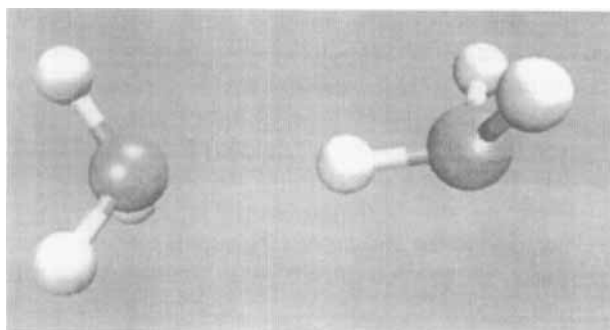
The density functional calculations are performed using procedures based on the Kohn-Sham formalism.<sup>35</sup> In the same way as in Hartree-Fock (HF) procedures, a matrix equation of the form

$$FC = ESC \quad (1)$$

is solved. The expression for the Fock matrix

$$F = T + V + V_C + V_{XC} \quad (2)$$

contains the kinetic ( $T$ ), the electron-nuclear attraction ( $V$ ), and the electron repulsion ( $V_{xc}$ ) operators as usual. Different expressions have been used for the computation of the exchange-correlation potential,  $V_{xc}[\rho(\vec{r}), \vec{r}]$ .<sup>36</sup> In the linear combination of Gaussian-type orbitals-local spin density (LCGTO-LSD) method, they have been repre-



**FIGURE 1.** The global minimum, the linear structure of the ammonia dimer.

sented as<sup>37</sup>:

$$(V_{xc})_{ij} = \sum_n \chi_i(\vec{r}_n) * V_{xc}[\rho(\vec{r}); \vec{r}_n] \chi_j(\vec{r}_n) \bar{\omega}(\vec{r}_n) \quad (3)$$

where  $\chi_i$  are the GTOs,  $\bar{\omega}(\vec{r}_n)$  is the weighting factor at the sample point  $\vec{r}_n$  on a grid and  $\rho(\vec{r})$  is the electronic density of which the exchange-correlation potential is a functional. The calculations have been performed using the program package deMon developed by Salahub and coworkers<sup>38,39</sup> and the DFT implementation in the Gaussian 92 program package.<sup>40</sup> Different exchange correlation functionals were employed in the calculations, the Slater-<sup>41</sup> and the Becke-exchange potential,<sup>42</sup> the VWN,<sup>43</sup> the Perdew,<sup>44,45</sup> and the LYP<sup>46</sup> correlation functional. The correlation functionals were mainly combined with the Becke-exchange potential. The hydrogen bond energies were corrected in this article with the Boys-Bernardi counterpoise method<sup>29-31</sup> and with the CHA method<sup>31-34</sup> which was recently included in the deMon program package. Throughout these calculations performed with deMon we used the (631/31/1) and (31/1) basis sets for oxygen and hydrogen, respectively. The auxiliary bases were (5, 2; 5, 2) and (5, 1; 5, 1) for oxygen and hydrogen, respectively.

Several different definitions have been suggested by different researchers (7-point CP, use of only virtual orbitals of the second monomer, etc.).<sup>29,31</sup> We used in our investigations two CP methods, the 3-point and the 7-point method. Whereas the 3-point method corrects only for the basis set (the monomer energies are calculated in the dimer basis assuming the dimer geometry), the 7-point method also takes into account the geometrical differences between the monomer in the dimer structure and the free monomer.

A CHA/DFT theory was recently reported which has introduced modifications to the usual DFT-Fock matrix.<sup>34</sup> The basic idea of these corrections is to avoid the delocalization of the electrons of one monomer to the orbitals of the other monomer within the dimer. Based on density, which is the part of the electronic density assigned solely to monomer A, a Kohn-Sham-Fock matrix  ${}^pF_A^{AA}$  can be built up in the  $m_A$ -dimensional monomer basis of A. The eigenvalue equation is then

$$F_A^{AA} c_i^A = \varepsilon_i^A S^{AA} c_i^A \quad (4)$$

Superscripts AA and A indicate that all the orbital indices considered belong to A. Consequently, the Fock matrix obtained with DFT can be thought of

as consisting of the four submatrices shown below. A completely similar set of equations can be written for  $B$ . Now, using the density for  $A$ , the Fock matrix,  ${}^{\rho}F_A$ , can be constructed for the whole dimer basis

$${}^{\rho}F_A = \begin{pmatrix} {}^{\rho}F_A^{AA} & {}^{\rho}F_A^{AB} \\ {}^{\rho}F_A^{BA} & {}^{\rho}F_A^{BB} \end{pmatrix} \quad (5)$$

where subscript  $A$  indicates that this is a "ghost-orbital"-type Fock matrix built by only using  $\rho_A$ . Although only orbitals centered in  $A$  have been used for building  ${}^{\rho}F_A$ , the eigenvectors of the equation

$${}^{\rho}F_A c_i = \varepsilon_i S c_i \quad (6)$$

will not, in general, be localized on  $A$ . An exception to this is the case where  ${}^{\rho}F_A^{BA}$  is related to  ${}^{\rho}F_A^{AA}$  in the following way:

$${}^{\rho}F_A^{BA} = S^{BA} (S^{AA})^{-1} {}^{\rho}F_A^{AA} \quad (7)$$

A possible way of correcting BSSE at the level of finite-basis Kohn–Sham equations is to substitute the conventional Fock matrix with a corrected one:

$${}^{\rho}F_{CHA} = {}^{\rho}F + \begin{pmatrix} 0 & S^{AB} (S^{BB})^{-1} {}^{\rho}F_B^{BB} - {}^{\rho}F_B^{AB} \\ S^{BA} (S^{AA})^{-1} {}^{\rho}F_A^{AA} - {}^{\rho}F_A^{BA} & 0 \end{pmatrix}$$

The geometries investigated in this work are shown in Figure 1. To examine the two cyclic structures, the asymmetric "microwave" and the centrosymmetric one, we performed optimizations of the intermolecular parameters with the DFT method using the Becke-exchange,<sup>42</sup> the LYP-correlation potential,<sup>46</sup> and the MP2 method. Starting with the geometry obtained from these optimizations we performed full optimizations, and also relaxing the intramolecular parameters. Throughout our calculations we used the 6-31 + G( $d$ ,  $p$ ), the 6-31 + G(2 $d$ , 2 $p$ ), and the 6-311 ++ G(2 $df$ , 2 $pd$ ) basis sets.

## Results and Discussion

As previously mentioned, our investigations aim to compare DFT calculations, using various exchange and correlation potentials, with *ab initio* results at the MP2 level in the very sensitive case of ammonia dimers. We performed geometry optimizations of the ammonia monomer and the dimers assuming linear (Fig. 1) and centrosymmetric cyclic (Fig. 2) structures for the complex. These

two structures were determined to be the minima on the potential energy surface, calculated by Latajka and Scheiner.<sup>17</sup> The geometries of the optimized cyclic and linear dimer, as well as the geometry of the optimized monomer, are shown in Table I. The most striking differences among all geometric parameters listed for the dimer concern the intermolecular N—N distance. This is in agreement with the general finding that intermolecular parameters are much more dependent on the potential used than are the intramolecular ones. The range of N—N distances spans from 2.91 Å for Slater-exchange VWN (SVWN) to 3.503 Å for Becke-exchange VWN (BVWN), whereas the range for the N—H bond distances is much smaller (1.016 Å to 1.023 Å). With respect to the intermolecular distances, the results can be divided in two groups, the first one being that of local potentials and the second being that of gradient-corrected ones. Whereas nearly all gradient-corrected potentials give N—N distances comparable to MP2 results,<sup>3,4,6</sup> the local potential predict N—N distances to be about 0.2 Å too short. The best result is provided by the BLYP potential (3.335 Å, assuming linear structure) which gives closest agreement

with both the MP2 result (3.332 Å, assuming linear structure) and the experiment (3.337 Å).<sup>15</sup> The close agreement between the experimental N—N distance and the calculated BLYP and MP2 values supports the theoretical investigations which assumed that the ammonia complex forms a linear hydrogen bond.<sup>8–13,17,18</sup> This result is further substantiated by the hydrogen-bonding energies for the linear and the cyclic structure which are shown in Table II and which clearly indicate a preference for the linear structure.

The hydrogen-bond and total energies of the monomers and dimers are summarized in Table II.

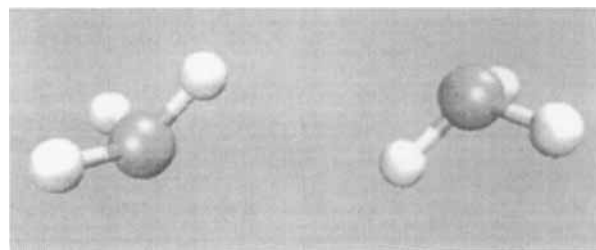


FIGURE 2. The cyclic structure of the ammonia dimer.

TABLE I.

The Geometrical Parameters of the Centrosymmetric Cyclic and Linear Ammonia Dimers and of the Monomer, Respectively, Obtained Using the Atomic Basis Set 6-311 + G(2d, 2p) Within the MP2 Method and DFT. The Slater- and Becke-Exchange Functionals Are Combined with the Vosko-Wilk-Nusair, the Perdew, and the Lee-Yang-Parr Correlation Functionals, Respectively.

	SVWN	BVWN	BP	BLYP	MP2
Monomer					
$r_{(N-H)}$	1.021	1.016	1.023	1.022	1.0091
$\angle_{(H-N-H)}$	107.3	106.7	106.3	106.7	107.1
Dimer					
$C_{h2} r_{(N-N)}$	2.913	3.503	3.182	3.266	3.183
$C_s r_{(N-N)}$	2.996	3.507	3.267	3.335	3.322
$C_{h2} r_{(N-H1)}$	1.027	1.017	1.025	1.026	1.010
$C_s r_{(N-H1)}$	1.035	1.023	1.031	1.031	1.014
$C_{h2} r_{(N-H2)}$	1.021	1.016	1.023	1.023	1.012
$C_s r_{(N-H2)}$	1.021	1.016	1.023	1.023	1.010
$C_{h2} \theta 1$	41.1	43.7	42.7	43.3	42.4
$C_s \theta 1$	6.4	7.9	8.3	8.0	5.8
$C_{h2} \theta 2$	41.1	43.7	42.7	43.2	42.7
$C_s \theta 2$	121.8	128.0	128.2	128.1	
$C_{h2} \Delta(r_{N1}-r_{N2})$	0.006	0.001	0.002	0.003	0.002
$C_s \Delta(r_{N1}-r_{N2})$	0.014	0.007	0.008	0.008	0.004

The hydrogen-bond energies have been corrected with the 3-point (BB3) and the 7-point (BB7) Boys-Bernardi counterpoise method. The uncorrected interaction energies are also shown in Table II. Several observations can be made. The first method concerns the interaction energies calculated with different exchange-correlation functionals. The gradient-corrected exchange-correlation potentials are provided counterpoise-corrected (BB7) interaction energies of 2.4 (BP) and 2.3 kcal/mol (BLYP) for the linear structure, which

are in reasonable agreement with the experimental result of less than 2.8 kcal/mol.<sup>15</sup> On the other hand, the local SVWN correlation potential predicts a hydrogen-bond energy of about -5.3 kcal/mol, double the value of the gradient-corrected BLYP and BP potentials. The behavior of the SVWN potential is not surprising at all. The overbinding properties of the local SVWN potential have been described for a large variety of molecules, e.g., for metal complexes,<sup>49,50</sup> and is also reflected on the N—N distance, which is far

TABLE II.

The Total Energies of the Ammonia Monomer, the Linear, and the Centrosymmetric Cyclic Dimers, Respectively, (in a.u.) As Obtained from MP2 and DFT Calculations Using a 6-311G + (2p, 2d) Basis Set.<sup>a</sup>

		SVWN	BVWN	BP	BLYP	MP2
$E$ (monomer)						
$E$ (dimer)		-56.293002	-57.059390	-56.5844419	-56.559400	-56.433385
$\Delta E$ (uncorrected)	$C_{h2}$	-112.596103	-114.120675	-113.172319	-113.122153	-112.871856
	$C_s$	-112.596143	-114.121086	-113.172931	-113.122654	-112.871721
$\Delta E$ (BB3)	$C_{h2}$	-6.24	-1.17	-2.15	-2.10	-3.19
	$C_s$	-6.27	-1.43	-2.52	-2.43	-3.11
$\Delta E$ (BB7)	$C_{h2}$	-5.53	-1.10	-2.04	-2.01	—
	$C_s$	-5.51	-1.39	-2.42	-2.35	—
$\Delta E$ (BB7)	$C_{h2}$	-5.30	-1.10	-2.04	-2.02	—
	$C_s$	-5.30	-1.38	-2.41	-2.34	—

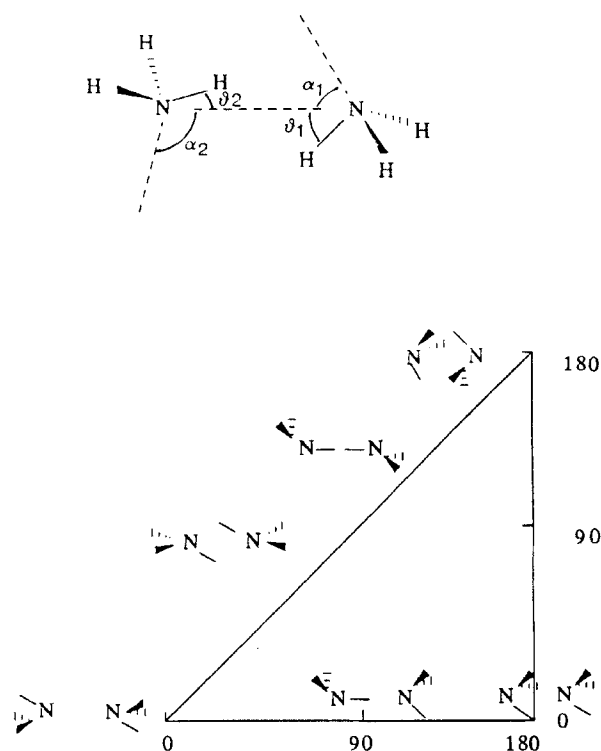
<sup>a</sup> The hydrogen-bond energies (in kcal/mol) of the DFT calculations are corrected for the BSSE with the 3-point and the 7-point Boys-Bernardi counterpoise method.

too small (2.91 Å). The exceedingly large interaction energy is due to the Slater-exchange potential, since a value of  $-1.4$  kcal/mol was calculated if the Becke-exchange potential is used with the VWN correlation functional.

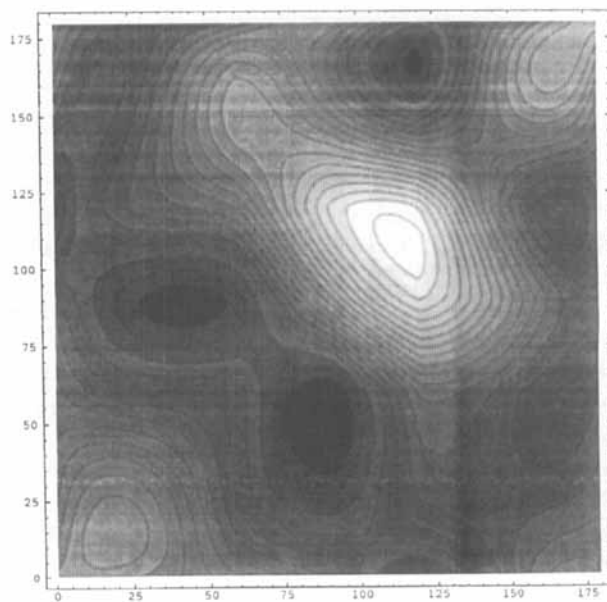
The second observation concerns the energy differences between the centrosymmetric and the linear structure of the ammonia dimer. All methods agree in the prediction of the linear structure to be the minimum, although the energy difference between both structures is rather small. The energy differences between both structures range from 0.37 kcal/mol to 0.03 kcal/mol, calculated with BP and SVWN, respectively.

The last observation concerns the counterpoise corrections, as suggested first by Boys and Bernardi,<sup>29</sup> and later modified by Mayer et al.<sup>31</sup> As seen in Table II, the BB3 correction (performed for the monomers assuming dimer geometry) predicts nearly the same basis set superposition error (BSSE) than the more costly BB7 correction (which takes into account the geometrical difference between monomer and dimer). The largest BSSE is found in the case of the SVWN potential. The counterpoise correction improves this result drastically, but even taking BSSE into account the result remains far from the experimental or MP2 value.

To analyze the exchange and the correlation energy contributions of the BLYP and the BVWN potentials to the total energy of the linear ammonia complex, we calculated the energy curve of the dimer as a function of the intermolecular distance (varying the N—N distance from 3.0 to 3.9 Å). With the exception of the N—N distance, all the other geometry parameters in the dimer were kept fixed. Since the geometrical parameters change only marginally when changing the basis set from 6-311G + (2*d*, 2*p*) to 6-311G(2*d*, 2*p*), the energy curves of Figures 3 and 4 were done using the smaller set. In Figure 3, the total energy curves around the minimum of the ammonia dimer are presented. The exchange energy obtained with the Becke-exchange potential is added to the Hartree energy to give the Hartree-Fock (HF) result within the framework of the density functional theory. Finally, the addition of the correlation energy calculated with the LYP-correlation potential to the HF results in the correlated total energy (DFT/BLYP). Two energy curves are displayed to compare the results obtained within DFT when using the Becke-exchange potential with the results obtained when HF (HFB) calculations are performed. It seems that the HFB curve in Figure 3 shows no minimum. In fact the minimum lies at



**FIGURE 3.** The Hartree-Fock (HF), the Hartree-Fock-Becke-exchange (HFB) and the Hartree-Becke-exchange/Lee-Yang-Parr correlation (BLYP) potential energy curve of the linear ammonia dimer calculated using a 6-311G(2*d*, 2*p*) basis set.

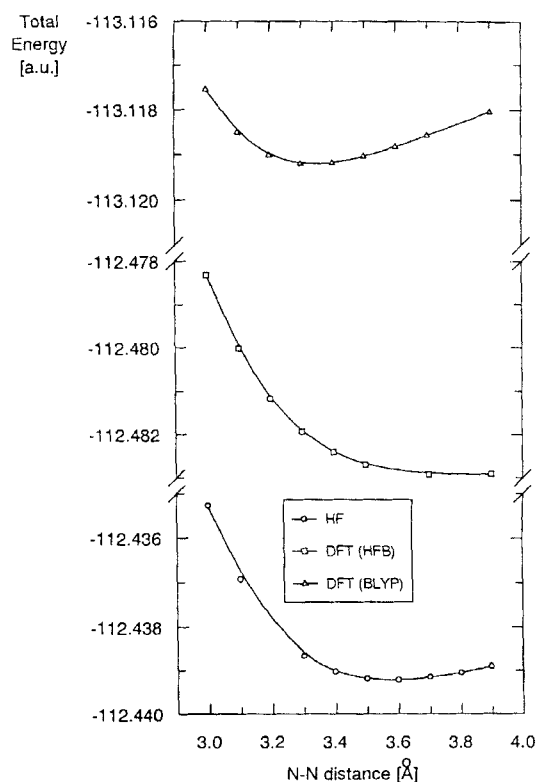


**FIGURE 4.** The correlation energies of the linear ammonia dimer obtained with MP2, the Vosko-Wilk-Nusair and the Lee-Yang-Parr correlation functionals, respectively. The energies were calculated with a 6-311G(2*d*, 2*p*) basis set.

3.8 Å, quite far from the HF value of 3.6 Å. The elongation of intermolecular bond lengths with the Becke-exchange potential has already been noticed for other complexes, for instance, in the water dimer.<sup>48</sup> similar to the N—N distance of the ammonia dimer, the Becke-exchange potential elongates to O—O distance of the water dimer by about 0.2 Å with respect to HF result. The too-repulsive behavior of the Becke-exchange potential is corrected by inclusion of correlation as shown in Figure 4.

The correlation energies calculated with the LYP and the VWN correlation potentials are presented together with the MP2 results in Figure 4. The LYP correlation has been chosen as an example of the gradient-corrected correlation potentials, whereas the VWN potential does not include gradient corrections. As it can be seen in Figure 4, the curve obtained with the VWN-correlation potential is considerably flatter than the curves obtained when using the LYP-correlation potential or MP2. As mentioned previously, result provided by the BLYP potential is in close agreement with the MP2 result and experiment. Whereas BLYP is able to predict the intermolecular distance correctly (3.335 Å) the BVWN potential elongates this bond considerably (3.503 Å).

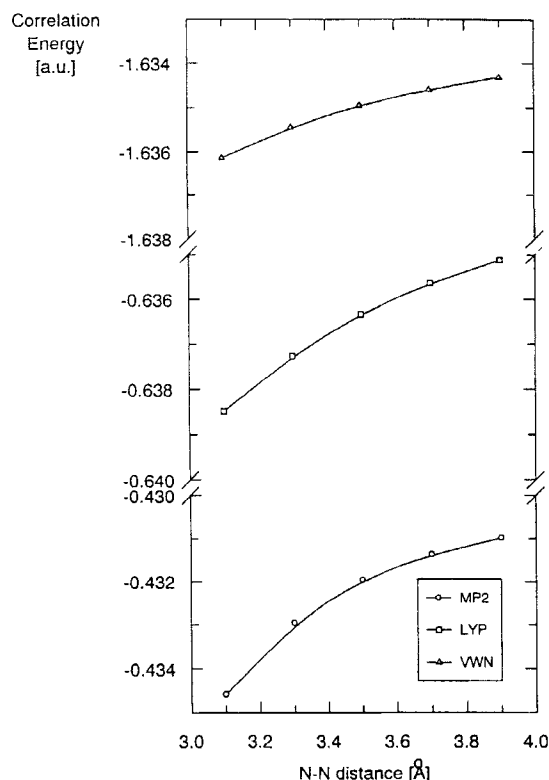
To investigate DFT with respect to its ability of describing rotational movements in the ammonia dimer, the potential energy surface of the dimer was calculated. This was done using the Becke-Perdew potential as implemented in the deMon program<sup>34</sup> with the [6311/311] basis set for nitrogen and the [311/1] basis set for hydrogen. Similar to the work of Latajka and Scheiner,<sup>17</sup> the energy surface was defined to be only a function of two rotational angles,  $\alpha_1$  and  $\alpha_2$ , as shown in Figure 5. Ranging from 0° to 180°, the search space contains all chemically noteworthy conformations of the complex, such as the linear configuration, which occurs at values around 112° for  $\alpha_1$  and 0° for  $\alpha_2$  (this corresponds to a value of about 4° for  $\theta_1$ ) as well as the asymmetric cyclic structures with rotational angles which show values ranging from 50° to 80° (this corresponds to values of about 60° to 30° to  $\theta_1$  and 2) and at last the trifurcated structure of the dimer as explained in Figure 5. The intramolecular distances in the ammonia monomers were held fixed at the N—H bond lengths of 1.025 Å. The H—N—H bond angles in the monomers amount to 107.5°. These values were optimized within the LDA procedure using the local potential. The surface was investigated at a fixed intermolecular distance of 3.2 Å.



**FIGURE 5.** Various structures of the ammonia dimer. Superscripts 1 and 2 are defined as the angles between the intermolecular axis and the  $C_3$  symmetry axes of the ammonia monomers, respectively.

The contours of Figure 6 are separated from each other by 0.5 kcal/mol with an interaction energy for the linear minimum structure of about -4.37 kcal/mol. The interaction energies of the potential surface are not corrected for the BSSE. As described by Latajka and Scheiner, the contour map shows a very shallow valley connecting the linear  $C_s$  structure with the cyclic  $C_{h2}$  structure.<sup>17</sup> The topology of the potential contour map found here is in good agreement with the potential energy surface calculated by Latajka and Scheiner at the Hartree-Fock level using a 4-31G\* basis set.<sup>17</sup> The other minimum structure of the potential surface belongs to a trifurcated structure similar to the cyclic  $C_{h2}$  one. In one of the ammonia units two hydrogens (instead of one) are pointing toward the neighboring ammonia monomer in the cyclic structure.

Since the potential energy surface suggests that the centrosymmetric structure is a transition state between the two asymmetric structures, we investigated whether one of the bifurcated cyclic structures (centrosymmetric and asymmetric) belongs



**FIGURE 6.** Potential energy surface for the ammonia dimer calculated with Becke–Perdew using a [6311/31/1] basis set for oxygen and a [311/1] basis set for hydrogen. The variable of the vertical axis is 2 and the variable of the horizontal axis is 1, as shown in Figure 2. The contour lines designate the hydrogen-bonding energies of the dimer. They are separated by 0.5 kcal/mol, the largest value of the hydrogen-bonding energy is  $-4.37$  kcal/mol.

to a real minimum (as suggested by the experimental work of Klemperer et al.<sup>14–16</sup>) or to a transition state. For that purpose we optimized only the intermolecular parameters of the cyclic structures (the intramolecular monomeric parameters

were kept fixed). This was done since the microwave spectrum was interpreted assuming rigid monomers. Optimizing only intermolecular bond lengths and angles we had the same prerequisites in our calculations as in the experiment. We started with a centrosymmetric and an asymmetric cyclic structure. Both rotational angles ( $\alpha_1$  and  $\alpha_2$ ) and the intermolecular distances have been optimized using the BLYP correlation potential and a 6-311 + G(2d,2p) basis set. The intramolecular distances and angles were kept fixed at the values of the geometry-optimized ammonia monomer. The total energies calculated of both cyclic structures, as well as the intermolecular geometrical parameters, are shown in Table III. As can be seen in Table III, the energy difference between both structures is, with a value of 0.00002 a.u., negligible.

We determined the second derivatives of the energy for both cyclic structures (with optimized intermolecular parameters) for verifying the hypothesis that the centrosymmetric structure belongs to a transition state between the asymmetric cyclic minima. We did not find any negative eigenvalues of the force constant matrix in the asymmetric cyclic structure. On the other hand, only positive eigenvalues could be detected again in the case of the centrosymmetric cyclic structure. Therefore, these results (no negative eigenvalues) contradict the hypothesis of a centrosymmetric transition state or saddle point on the potential energy surface. Thus, our DFT calculations, assuming rigid monomers, are in agreement with the MP2 results of Latajka and Scheiner,<sup>17</sup> who stated that the centrosymmetric cyclic structure belongs to a minimum. Moreover, they explain the large dipole moment found in the ammonia dimer to be caused by large vibrational averaging and not due to the existence of stable asymmetric cyclic minima. To verify that the asymmetric cyclic structures do not belong to minimum structures, we

**TABLE III.**  
The Optimized Intermolecular Parameters in Both Cyclic Ammonia Dimer Structures, the Asymmetric "Microwave" and the Centrosymmetric Structure, Respectively.<sup>a</sup>

	MP2 asymmetric	MP2 symmetric	BLYP asymmetric	BLYP symmetric
$r_{(N-N)}$	3.188	3.185	3.199	3.198
$\theta_1$	37.0	42.3	47.6	43.2
$\theta_2$	48.3	42.7	49.0	43.1
Total energy	-112.871846	-112.871837	-113.122144	-113.122084

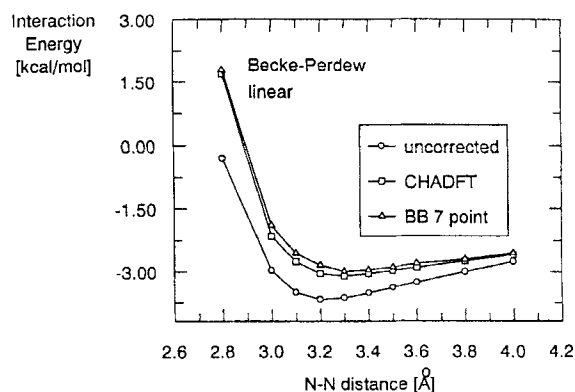
<sup>a</sup> MP2 and DFT with the BLYP potential have been used. The N—N distance is given in angstroms and the angles in degrees. The total energies are given in atomic units.



performed, in a third calculation, a full optimization (including intramolecular parameters) starting from the two partially optimized cyclic structures (the centrosymmetric and the asymmetric ones assuming rigid monomers). The centrosymmetric structure kept its configuration, whereas the asymmetric cyclic structure passed to the linear one.

Previous publications on DFT applications presume that the quality of the DFT results using gradient-corrected exchange-correlation potentials are comparable to MP2 results.<sup>3,4</sup> Therefore, we checked whether our results on the cyclic structures obtained within the DFT could be verified at the MP2 level using the same basis set as in DFT. Parallel to the DFT investigations described in the previous section we performed the intermolecular geometry optimization of both cyclic structures, centrosymmetric and the asymmetric, again under the constraint of rigid monomers. The results are depicted in Table III. We also calculated the second derivatives at the cyclic structures optimized for the intermolecular parameters. No qualitative differences could be found between the two methods, DFT and MP2. As in the case of the DFT calculations, the MP2 method indicated that the centrosymmetric, as well as the asymmetric, structure are real local minima with respect to the intermolecular parameters. In close agreement with the DFT calculations, the MP2 differences of the total energies between both cyclic structures (asymmetric and centrosymmetric) are negligible and the eigenvalues of the force constant matrix are all positive. Moreover, full optimization starting at the partially optimized structures gave the same qualitative results as the DFT calculations. As in the DFT calculations, the centrosymmetric structure remained during the optimization within MP2, whereas the asymmetric cyclic structure turned into a linear configuration.

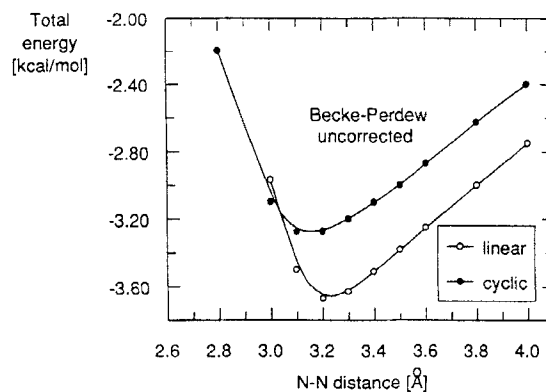
Since Tao and Klemperer<sup>25</sup> stressed that, especially in the case of the ammonia dimer, the correction of the BSSE can be of great importance for determining that the cyclic structure is the energetically preferred configuration, we paid special attention to hydrogen bond energies and the corrections for the BSSE (Table II, Figs. 7–9). The fact that it is not possible to perform a geometry optimization, including counterpoise corrections for the BSSE (since these corrections are performed “*a posteriori*”), forced Tao and Klemperer<sup>25</sup> to perform an optimization at the MP2 level by determining the potential curves of the intermolecular N—N distance stepwise “by hand” (in the same



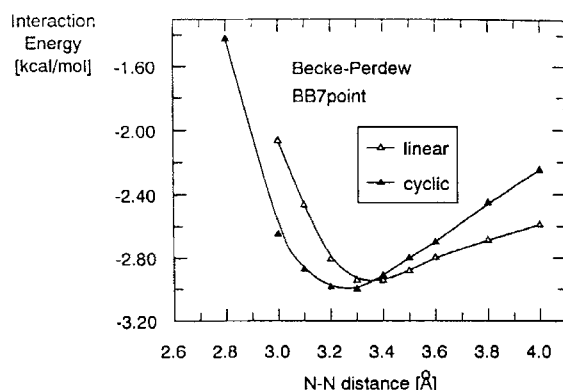
**FIGURE 7.** The hydrogen-bond energies of the linear ammonia dimer, corrected with the BB7-point and the CHA/DFT method. The Becke-Perdew potential with a DZVP basis set was used. To compare these results with the uncorrected ones, the latter ones are also depicted.

way they determined the potential curve for the N—H bond length and the intermolecular rotational angles). Using this method they obtained a centrosymmetric cyclic structure, which is energetically preferred to the linear structure by about 0.02 kcal/mol.

Inspired by the Tao and Klemperer<sup>25</sup> procedure we determined the potential energy curves of the ammonia dimer by varying stepwise the intermolecular N—N distance of the linear and the centrosymmetric cyclic structure. The geometrical parameters of the dimer and the monomer were optimized using the Becke-Perdew (BP) potential with a 6-31 + G(*d*, *p*) basis set. We calculated the potential curves using a step size of 0.1 Å for the



**FIGURE 8.** The uncorrected hydrogen-bond energies of the linear and the centrosymmetric cyclic ammonia dimer structures. The Becke-Perdew potential with a DZVP basis set was used.



**FIGURE 9.** The BB 7-point-corrected hydrogen-bond energies of the linear and the centrosymmetric cyclic ammonia dimer structures. The Becke–Perdew potential with a DZVP basis set was used.

N—N distance (all the other intra- and inter-monomer geometrical parameters were kept fixed at the optimized dimer structure). As an example of the different possibilities for correcting the BSSE (*a posteriori* via the BB7 method and *a priori* via the CHA approach) the corrected and the uncorrected interaction energy curves of the linear dimer using the BP potential are depicted in Figure 7.

It is evident from Figure 7 that the difference between the CHA and CP BB 7-point curves is smaller than between the CP-corrected DFT curve and the uncorrected one. As in the case of the CHA implementation into HF and correlated methods by Mayer et al.<sup>31–33</sup> the CHA curve lies between the uncorrected and the BB 7-point-corrected curves. Moreover, the CHA and the BB 7-point-corrected curves are melting together at larger distances, as it has been described for HF.<sup>31–33</sup>

Further observations concerning the correction of the BSSE and its consequences for predicting the equilibrium structure can be made comparing Figure 8 with Figure 9. Figure 8 shows the uncorrected hydrogen-bond energies of the linear and the centrosymmetric cyclic structure, whereas Fig-

ure 9 provides the same results obtained with the BB 7-point correction. As it can be seen in Figure 9, the Boys–Bernardi counterpoise correction predicts the cyclic structure to be the energetically preferred one, a result in close agreement with Tao and Klemperer,<sup>25</sup> who determined a difference of about 0.02 kcal/mol, preferring the centrosymmetric cyclic structure. Employing the BB 7-point correction, our DFT hydrogen-bond energy of the centrosymmetric structure is about 0.06 kcal/mol lower than the one of the linear structure, whereas the uncorrected energies predict an energy difference of about 0.4 kcal/mol, preferring the linear configuration. This difference may be due to overcompensation of the energy difference of about 0.6 kcal/mol between the cyclic and the linear structure with the BSSE about 1 kcal/mol (found at the potential energy minimum of the linear structure in Fig. 7). It can be expected that the BSSE of the cyclic structure will be somewhat larger than the BSSE of the linear one due to the smaller intermolecular N—N distance of the cyclic configuration.

In Table IV we show the basis set dependence on the energy difference between the cyclic and the linear structure using the BLYP potential. The expansion of the basis set from 6-31G + (*d*, *p*) to 6-311G ++ (2*df*, 2*pd*) does not change the result than the linear structure is the energetically preferred one. In Table IV, we included MP2 and MP4SDTQ results using the 6-311G + (2*d*, 2*p*) basis set. Comparison of the MP2 and MP4SDTQ results with DFT shows that the linear structure remains to be the global minimum structure of the ammonia dimer.

## Conclusions

In general, all DFT potentials investigated reflect the fact that the linear structure of the ammonia dimer is the energetically preferred confor-

**TABLE IV.** The Total Energies (a.u.) of the Centrosymmetric Cyclic and the Linear Structure of the Ammonia Dimer as Obtained From MP2 and MP4 Calculations with a 6-311 + G(2*d*, 2*p*) Basis Set and from DFT Calculations Using the Becke–Exchange Lee–Yang–Parr–Correlation Potential with Three Different Basis Sets.

	BLYP			MP2	MP4SDTQ
	6-31 + G( <i>d</i> , <i>p</i> )	6-311 + G(2 <i>d</i> , 2 <i>p</i> )	6-311 ++ G(2 <i>df</i> , 2 <i>pd</i> )	6-311 + G(2 <i>d</i> , 2 <i>p</i> )	6-311 + G(2 <i>d</i> , 2 <i>p</i> )
C <sub>s</sub>	−113.083602	−113.122654	−113.124883	−112.87172	−112.910375
C <sub>h2</sub>	−113.083204	−113.122153	−113.124275	−112.871856	−112.910446

mation. This is in agreement with the results of Latajka and Scheiner,<sup>17</sup> Frisch et al.,<sup>23,24</sup> and also with those of Klemperer and Tao,<sup>25</sup> when employing no midbond functions. Although all three of the potentials investigated behave qualitatively correctly, the best results with respect to the hydrogen-bond energies are found using either the Becke–Perdew (2.4 kcal/mol) or the Becke–Lee–Yang–Parr (2.3 kcal/mol) potential. The best results with respect to the intermolecular distance are found with the Becke–Lee–Yang–Parr potential. As already found in other dimers involving hydrogen bonds, the local potential gives a value which is much too high for the hydrogen-bond energy.<sup>3–7</sup> This is true for both structures, the cyclic as well as the linear one, due to the exchange part of the potential as discussed above. Parallel to this effect, a considerable shortening of the N—N distances in both the linear and the cyclic structures is found.

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## References

1. J. A. Pople, P. M. W. Gill, and B. G. Johnson, *Chem. Phys. Lett.*, **169**, 387 (1990), and references therein.
2. B. G. Johnson, P. M. W. Gill, and J. A. Pople, *J. Chem. Phys.*, **97**, 7846 (1992).
3. F. Sim, A. St-Amant, I. Papai, and D. R. Salahub, *J. Am. Chem. Soc.*, **114**, 4391 (1992).
4. K. Laasoonen, M. Parrinello, R. Car, C. Lee, and D. Vanderbilt, *Chem. Phys. Lett.*, **207**, 208 (1993).
5. C. Mijoule, Z. Latajka, and D. Borgis, *Chem. Phys. Lett.*, **208**, 364 (1993).
6. T. Zhu and W. Yang, *Int. J. Quant. Chem.*, **49**, 613 (1994).
7. M. Kieninger and S. Suhai, *Int. J. Quant. Chem.*, **52**, 465 (1994).
8. W. L. Jorgensen and J. Ibrahim, *J. Am. Chem. Soc.*, **102**, 3309 (1980).
9. A. Hincliffe, D. G. Bounds, M. L. Klein, I. R. McDonald, and R. Righini, *J. Chem. Phys.*, **74**, 1221 (1981).
10. K. Hirao, T. Fujikawa, H. Konishiand, S. Yamabe, *Chem. Phys. Lett.*, **104**, 184 (1984).
11. J. A. Pople, *Faraday Discuss. Chem. Soc.*, **73**, 7 (1982).
12. Z. Latajka and S. Scheiner, *J. Chem. Phys.*, **81**, 407 (1984).
13. J. E. Del Bene, *J. Chem. Phys.*, **86**, 2110 (1987).
14. G. T. Fraser, D. D. Nelson, Jr., A. C. Charo, and W. Klemperer, *J. Chem. Phys.*, **82**, 2532 (1985).
15. D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, *J. Chem. Phys.*, **83**, 6201 (1985).
16. D. D. Nelson, Jr., W. Klemperer, G. T. Fraser, F. J. Lovas, and R. D. Suenram, *J. Chem. Phys.*, **87**, 6364 (1987).
17. Z. Latajka and S. Scheiner, *J. Chem. Phys.*, **84**, 341 (1986).
18. D. M. Hassett, C. J. Marsden, and B. J. Smith, *Chem. Phys. Lett.*, **183**, 449 (1991).
19. K. I. Peterson, G. T. Fraser, D. D. Nelson, Jr., and W. Klemperer, In *Comparison of Ab Initio Quantum Chemistry with Experiment: State of the Art*, R. J. Bartlett, Ed., Reidel, New York, 1985.
20. K. Sagarik, R. Ahlrichs, and S. Brode, *Mol. Phys.*, **57**, 1247 (1986).
21. J. G. Loeser, C. A. Schuttenmaer, R. C. Cohen, M. J. Elrod, P. W. Steyert, R. J. Sajkally, R. E. Bumgarner, and G. A. Blake, *J. Chem. Phys.*, **97**, 4727 (1992).
22. J. W. I. van Bladel, A. van der Avoird, P. E. S. Wormer, and R. J. Saykally, *J. Chem. Phys.*, **97**, 4750 (1992).
23. M. J. Frisch, J. A. Pople, and J. E. Del Bene, *J. Phys. Chem.*, **89**, 3664 (1985).
24. M. J. Frisch, J. E. Del Bene, J. S. Binkley and H. F. Schaefer III, *J. Chem. Phys.*, **84**, 2279 (1986).
25. F.-M. Tao and W. Klemperer, *J. Chem. Phys.*, **99**, 5976 (1993).
26. Z. Latajka and S. Scheiner, *J. Comput. Chem.*, **8**, 663 (1987).
27. Z. Latajka and S. Scheiner, *J. Comput. Chem.*, **8**, 674 (1987).
28. J. E. Del Bene, *J. Comput. Chem.*, **10**, 603 (1989).
29. S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 558 (1970).
30. H. B. Jansen and P. Ross, *Chem. Phys. Lett.*, **3**, 140 (1969).
31. I. Mayer and P. R. Surjan, *Chem. Phys. Lett.*, **191**, 497 (1992).
32. I. Mayer and A. Vibok, *Int. J. Quant. Chem.*, **40**, 139 (1991).
33. P. Valiron, A. Vibok, and I. Mayer, *J. Comput. Chem.*, **14**, 401 (1993).
34. M. Kieninger, S. Suhai, and I. Mayer, *Chem. Phys. Lett.*, **230**, 485 (1994).
35. W. Kohn and L. J. Sham, *Phys. Rev. A*, **140**, 1133 (1965).
36. P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**, 648 (1964).
37. B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, *J. Chem. Phys.*, **71**, 3369, 4993 (1979).
38. D. R. Salahub, R. Fournier, P. Mlynarski, I. Papai, A. St-Amant, and J. Ushio, In *Theory and Applications of Density Functional Approaches to Chemistry*, J. Labanowski and J. Andzelm, Eds., Springer Verlag, Berlin, 1991.
39. A. St-Amant and D. R. Salahub, *Chem. Phys. Lett.*, **169**, 387 (1990).
40. Gaussian92/DFT, Revision G.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, P. L. Martin, D. J. Fox, D. J. Defrees,

- J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1993.
41. J. Slater, In *Quantum Theory of Matter*, McGraw-Hill, New York, 1951, Ch. 26.
42. A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
43. S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980).
44. J. P. Perdew and Y. Wang, *Phys. Rev. B*, **33**, 8800 (1986).
45. J. P. Perdew, *Phys. Rev. B*, **33**, 8822 (1986); Erratum in *Phys. Rev. B*, **38**, 7406 (1986).
46. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. A*, **34**, 785 (1986).
47. B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.*, **157**, 200 (1989).
48. O. N. Ventura, M. Kieninger, S. Suhai, and G. H. F. Diercksen, *J. Chem. Phys.*, (in press).
49. R. van Leeuwen and E. J. Baerends, *Int. J. Quant. Chem.*, **52**, 771 (1994).
50. T. Ziegler, *Chem. Rev.*, **91**, 651 (1991).